

Chapter 5

Continuous Monitoring of Nitrogen Dioxide

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Table of Contents

	Page
1.0 Introduction.....	1
2.0 Probe Siting Criteria.....	1
2.1 Horizontal and Vertical Probe Placement.....	1
2.2 Spacing from Obstructions.....	1
2.3 Spacing from Roads.....	1
2.4 Spacing from Trees.....	2
3.0 Monitoring Methodology.....	2
3.1 Chemiluminescent Measurement Method of NO ₂	2
3.2 Chemiluminescent Measurement Method of NO _y	3
4.0 Calibration Methodology.....	4
4.1 Permeation System (NO ₂).....	6
4.2 Blending and Dilution Systems (GPT).....	6
4.3 Certification Requirements.....	7
5.0 Analyzer Calibration Procedure.....	8
5.1 NO and NO _x (NO _y) Calibration Procedure.....	8
5.2 NO ₂ Calibration Procedure.....	19
6.0 Converter Efficiency Calculations.....	23
6.1 Calculation Procedure for Converter Efficiency.....	24
7.0 Regulator Purge Procedure.....	28
8.0 Quality Assurance Audits.....	29
8.1 Data Validation and Precision Audits.....	29
8.2 Accuracy Audits.....	36
9.0 Data Reduction and Reporting.....	37
10.0 Routine Station Operation.....	38
10.1 Station Checks.....	38
10.2 Analyzer Checks.....	38
10.3 Zero and Span Checks (Level 2 Checks).....	40
11.0 Equations.....	40
12.0 Requirements and Definitions.....	42

FIGURES

1. Analyzer Flow Diagram.....	5
2. Converter Efficiency.....	27

FORMS

1. NO/NO ₂ /NO _x Calibration Form (blank).....	11
2. NO/NO ₂ /NO _y Calibration Form (blank).....	12
3. Converter Efficiency-NO _x (blank).....	25
4. Converter Efficiency-NO _y (blank).....	26
5. NO _x Audit Form (blank).....	30

TABLES

1. Minimum Separation Distance Between Neighborhood Scale NO ₂ Monitoring Stations and Roadways.....	2
2. Example Data for Linear Regression.....	18
3. Required Concentrations for Precision and Accuracy.....	37
4. NO and NO ₂ Titration Concentrations.....	37

1.0 Introduction

This chapter outlines the requirements for the ambient air monitoring of oxides of nitrogen (NO, NO₂, and NO_x) and total reactive oxides of nitrogen (NO_y). The requirements stated in this chapter are to be followed by all organizations (e.g. State, local, industrial, and consultant) that conduct ambient air monitoring in Indiana and report data to the Air Quality System (AQS).

This chapter does not replace the analyzer's operation manual. The analyzer's operation manual should be read before any analyzer calibration, audit, or maintenance is performed. The operation manual should be available at the monitoring station as a reference guide.

2.0 Probe Siting Criteria

For specific probe siting and spatial scales of representation, refer to the Code of Federal Regulations (CFR) 40, Part 58, Appendix E. In general, probe siting must meet the following requirements:

2.1 Horizontal and Vertical Probe Placement

1. The probe inlet (sample inlet) must be at a height of 3 to 15 meters above ground level.
2. The probe inlet must be more than 1 meter vertically and horizontally away from any supporting structure.
3. For NO_y, the catalytic converter must be positioned at a program specific height above ground level within the range of 3 to 15 meters as required for enhanced ozone monitoring programs.

2.2 Spacing from Obstructions

1. The distance between an obstacle and the inlet probe must be at least twice the height that the obstacle protrudes above the inlet probe (2 X rule).
2. Inlet probe placement extending out from a vertical wall is undesirable because air moving along that wall may be subject to removal mechanisms of NO₂.
3. Airflow must be unrestricted in an arc of 270° around the inlet probe. The predominant wind direction must be included within the 270° arc of inlet probe airflow.

2.3 Spacing from Roads

1. The probe inlet should be placed far enough away from any NO₂ sources which could dominate (bias) the data (see Table 1 for separation distances).

2.4 Spacing from Trees

1. The inlet probe should be at least 20 meters from the drip line of trees. The drip line is defined as the point on the ground from where water will drip down from the outer most branches of the tree.
2. The inlet probe must be at least 10 meters from the drip line of trees if the trees protrude 5 meters or more above the probe.

Table 1
Minimum Separation Distance Between Neighborhood
and Urban Scale NO₂ Monitoring Station and Roadways
(Edge of Nearest Traffic Lane)

Roadway average daily traffic (vehicles/day)	Minimum separation distance between roadways and stations (meters)
< 10,000	> *10
15,000	20
20,000	30
40,000	50
70,000	100
< 110,000	> 250

* Distances should be interpolated based on traffic flow.

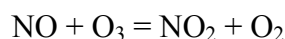
3.0 Monitoring Methodology

All methods used to monitor NO₂ must be an EPA reference or equivalent method as described in 40 CFR Part 50.1. Continuous ambient NO₂ analyzers must have an EPA reference method number posted on the analyzer or listed in the instrument manual. At present, EPA does not have a reference or equivalency requirement for NO_y.

3.1 Chemiluminescent Measurement Method of NO₂

The chemiluminescence measurement method is based on the reaction of ozone (O₃) with nitric oxide (NO) to form nitrogen dioxide (NO₂) (see Equation 5-1).

Equation 5-1



A typical ambient NO₂ analyzer determines concentrations of NO₂ by measuring NO and NO_x

concentrations. NO_x is defined as the sum of the NO_2 and NO analyzer measurements. The analyzer never directly measures NO_2 .

Equation 5-2

$$\text{NO}_2 + \text{NO} = \text{NO}_x$$

OR

$$\text{NO}_x - \text{NO} = \text{NO}_2$$

The analyzer ozonates an incoming ambient air sample (containing NO) to produce electronically excited NO_2 molecules. These molecules immediately decay to a lower energy level by emitting light (chemiluminescence) in the 600 nm to 2400 nm wavelength range. The intensity of the light generated is directly proportional to the concentration of NO in the ambient air sample. **The NO concentration of Equation 5-2 has now been measured.**

NO_x is measured by passing the air sample for part of the measurement cycle through a catalytic converter. Any NO_2 in the air sample is first reduced by the converter to NO . The NO already in the air sample is not affected by the converter. The reduced NO_2 and NO is then ozonated by the analyzer to produce the electronically excited (light emitting-chemiluminescent) NO_2 molecule. The intensity of light is measured by the analyzer and is reported as a NO_x concentration. **The NO_x concentration of Equation 5-2 has now been measured.**

Using Equation 5-2 the analyzer derives the concentration of NO_2 by subtracting the NO concentration from the NO_x concentration. Figure 1 shows the basic flow pattern of a typical $\text{NO}/\text{NO}_2/\text{NO}_x$ analyzer.

3.2 Chemiluminescent Measurement Method of NO_y

The same principle used for the measurement of NO , NO_2 , and NO_x is used for the total reactive oxides measurement by the nitrogen analyzer. The NO and NO_y concentrations are determined by photochemically measuring the light intensity at wavelengths greater than 600 nanometers from the chemiluminescent reaction of nitric oxide with ozone (see Equation 5-1). The primary differences between the configuration of the NO_y instrument and the EPA approved NO_2 instrument are the locations of the catalytic converter, particulate filter(s), flow control capillary, and the 3-way solenoid valve used for mode control.

To measure NO_y , sample air is passed through a probe-mounted catalytic converter. The nitroxyl compounds present are reduced to NO . The NO already in the air sample is not affected by the converter. The NO resulting from the reduction of these nitroxyl compounds, plus any native NO , is reactive with ozone. The resulting chemiluminescent light is measured as the total NO_y concentration. To measure NO separately and specifically, sample air is by-passed around the catalytic converter so that no reduction of the nitroxyl compounds to NO occurs.

The NO is reactive with the ozone and the resulting chemiluminescent light is measured as the NO concentration.

4.0 Calibration Methodology

The calibration method for a NO/NO₂/NO_x analyzer is based on the gas phase titration (GPT) between O₃ and excess NO to produce NO₂.

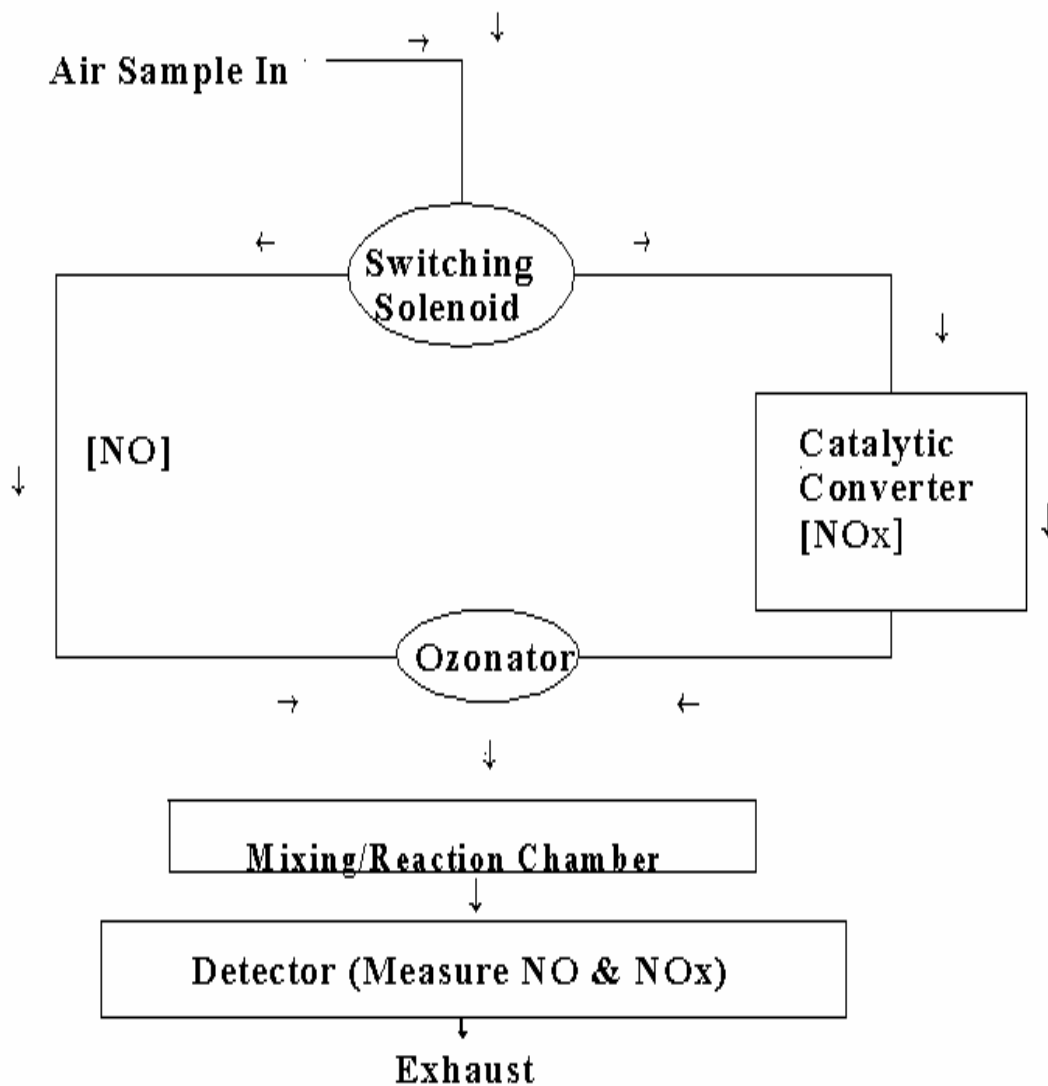
A high concentration cylinder of NO gas (approximately 50 parts per million, or ppm) is diluted with measured flows of zero (clean) air.

Zero air is defined as dilution air which is free of moisture and the pollutants being measured by the analyzer. For the NO/NO₂/NO_x calibration method, dilution air is cleaned or scrubbed of NO, NO₂, and O₃ with the following: a drying column of silica gel, an oxidizing catalyst column or ultra violet lamp to convert NO to NO₂, and a charcoal column for NO₂ and O₃ removal. This scrubbing method will remove NO, NO₂, and O₃ below the minimum detectable limits of the analyzer.

A known concentration of the diluted NO gas is titrated with concentrations of O₃ in order to produce NO₂ concentrations. When titrating NO with O₃, the changes in the calibrated NO channel are used to determine NO₂ concentrations (Equation 5-1). The example calibration (Figure 2, page 26) shows the changes in the NO channel and the produced NO₂ concentrations.

The calibration method for NO_y is similar to the calibration method of NO/NO₂/NO_x instruments. It uses the gas phase titration of an NO standard with O₃. When the NO concentration is known, the concentration of NO₂ can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO_y instrument is used as an indicator of changes in NO concentration. Upon the addition of O₃, the decrease in NO concentration observed on the calibration NO channel is equivalent to the concentration of NO₂ produced. The amount of NO₂ generated may be varied by adding variable amounts of O₃ from a stable O₃ generator. The NO_y catalytic converter is probe-mounted between the zero air sample and the instrument.

Figure 1
Analyzer Flow Diagram



4.1 Permeation System (NO₂)

NO₂ can also be produced using a permeation system. The permeation system is used to produce concentrations of NO₂ using a vial of NO₂ (with a known permeation rate) that is contained in a chamber or oven heated to a constant temperature. A flow of zero air is passed through this chamber and varying amounts of dilution air are then added in order to produce different concentrations of NO₂. The vial is under high pressure so the NO₂ is in a liquid state. Total flow through system is measured and used in Formula A to determine NO₂ concentration.

Formula A

$$\frac{\text{Perm Rate} \times .532}{\text{Total Flow}}$$

An NO₂ permeation system can be used for daily zero and span (Level 2) checks. (see Section 10.3).

An NO₂ permeation system **cannot** be used for data validation audits (Level 1), biweekly precision checks, or for accuracy audits (see Section 8.0). The Code of Federal Regulations (40 CFR Part 58 Appendix A) require a residual amount of NO when Level 1, precision checks, and audits are performed (see Section 8.1). This will determine the analyzer's ability to differentiate between NO and NO_x measuring capabilities. An NO₂ permeation system does not have the capability to provide this residual NO. However, it may help determine when a problem has occurred with the analyzer, thus reducing the amount of data that could be invalidated.

An NO₂ permeation system is also of limited use for calibrations since it cannot be used to calibrate the NO channel of the analyzer. The preferred system for calibration and auditing is the GPT blending/dilution system.

4.2 Blending and Dilution Systems (GPT)

A GPT system consists of a cylinder of NO (in an oxygen-free gas, usually nitrogen), an ozonator, and a dilution/blending system. Specific components of the GPT system are:

1. An air flow controller capable of maintaining and measuring constant air flows within $\pm 2.0\%$ of the standard flow. The flow controller may be a mass flow controller, rotameter, capillary, or pressure regulator (snubber) type.
2. An NO flow controller (made of nonreactive material, i.e. stainless steel) capable of maintaining and measuring constant flows within $\pm 2\%$ of the standard flow. The flow controller may be a mass flow controller, rotameter, capillary, or snubber type.
3. A pressure regulator for the cylinder of the NO standard gas which must be made of

nonreactive materials (i.e. stainless steel, Teflon). The regulator must be able to deliver NO at a suitable pressure. The regulator must have a CGA 660 cylinder connection fitting.

4. An ozone generator capable of generating sufficient, stable levels of O₃ for the GPT reaction with NO concentrations.
5. A shutoff valve (of nonreactive material) to stop the NO flow when zero air is required.
6. A reaction chamber (nonreactive material) for the quantitative reaction of O₃ with excess NO with sufficient volume to meet the residence requirements of 40 CFR Part 50, Appendix F, Section 1.4.
7. A mixing chamber (nonreactive material) designed to provide thorough mixing of the GPT reaction products and dilution air. The inlet and outlet should be of sufficient diameter so that the chamber is at atmospheric pressure under normal operation and sufficient turbulence must be created in the chamber to facilitate thorough mixing. Chamber Volumes in the range of 150 to 250 cm³ are sufficient.

NOTE: MOST COMMERCIALY MADE GPT BLENDING & DILUTION SYSTEMS HAVE A COMBINED REACTION AND MIXING CHAMBER. THE RESIDENCE REQUIRED HAS BEEN CALCULATED AND SHOULD BE LISTED IN THE OPERATION MANUAL.

8. An output manifold (nonreactive material) to provide a vented sample to the analyzer.
9. A cylinder of NO gas with less than 1 ppm NO₂ impurity certified by the Indiana Department of Environmental Management, Office of Air Quality, Quality Assurance Section (IDEM,OAQ,QAS).

See Chapter 6 of this manual, "Certification Methods for Transfer Standards".

The NO cylinder valve must be compatible with a CGA 660 regulator fitting.

10. A zero (clean) air system which is free of the contaminants of NO, NO₂, and O₃ (see Section 4.0).

4.3 Certification Requirements

Blending systems (GPT) used for audits and calibrations must be certified by the IDEM/OAQ/QAS at least every 6 months.

For blending systems with mass flow meters/controllers, this certification includes certifying the flow meters prior to the NO gas certification.

System recertification must be done immediately if any of the following conditions occur:

1. Major maintenance on the blending system (e.g. mass flow meter replacement)
2. Any unexplained problems with calibrations or audits that make calibrator output concentrations questionable
3. Replacement of the certified NO gas cylinder with a new cylinder

5.0 Analyzer Calibration Procedure

The calibration of one NO/NO₂/NO_x analyzer actually involves performing three calibrations; one calibration for each of the analyzer's three channels (see Form 1). While the NO and NO_x channels can be calibrated simultaneously, a typical GPT calibration may take 3 to 4 hours to complete. Because the principle, apparatus, and procedures used to calibrate the NO_y instrument are similar to the NO/NO₂/NO_x instruments, it may be possible to calibrate both types of instruments simultaneously. Since the procedures for the calibration of the NO/NO₂/NO_y analyzer are the same as the NO/NO₂/NO_x analyzer, the NO_x response is replaced with the NO_y response when referring to the NO/NO₂/NO_y analyzer calibration (see Forms 1 and 2).

The calibrated NO and NO_x channels of the analyzer indirectly determine NO₂ concentrations (see Equation 5-2).

NOTE: NO₂ IS NEVER DIRECTLY MEASURED. IN ORDER TO ACCURATELY MEASURE NO₂, THE NO AND NO_x CHANNELS MUST FIRST BE CALIBRATED ACCURATELY.

A data validation audit (Level 1) should be conducted prior to any routine recalibration. This one point audit must be conducted prior to any analyzer adjustments. The purpose of the audit is to determine the validity of the data from the last audit or calibration to the present date. See Section 8.0 for the audit procedure.

5.1 NO and NO_x (NO_y) Calibration Procedure

GPT techniques require the use of the NO channel of the analyzer and determine the amount of NO₂ generated through titration. When titrating NO with O₃, the changes in the calibrated NO channel determine the NO₂ concentrations.

It is necessary to calibrate and determine the linearity of the NO and NO_x (NO_y) channels before proceeding with the NO₂ calibration. The calibrated NO and NO_x (NO_y) channels of the analyzer will then indirectly determine NO₂ concentrations using Equation 5-2.

During the calibration, the analyzer must be operating in its normal sampling mode. The calibration gas must pass through all filters, scrubbers, conditioners, and other components used during the normal ambient sampling mode. All operational adjustments to the analyzer (i.e.

sample flow, PMT voltages, converter replacement, etc.) should be completed prior to the calibration.

Record all pertinent information on the calibration forms (i.e. see Forms 1 & 2).

NOTE: All NO/NO₂/NO_x and NO/NO₂/NO_y analyzers must be routinely calibrated at least once every six (6) months.

1. Record the station name and the AQS (Air Quality System) site identification number on the calibration form.
2. Identify the person performing the calibration (initials) and record the date of the calibration.
3. Record the analyzer's manufacturer name (brand), model number, and serial number.
4. Record the analyzer's initial settings: flows, vacuum, etc.
5. Record the GPT system (calibrator) manufacturer name, model number, and serial number.
6. Record the NO calibration gas cylinder number, the certified concentration, and the certification date.

NOTE: DO NOT USE CYLINDERS WITH PRESSURES < 200 PSIG (POUNDS PER SQUARE INCH GAUGE).

GASES MAY BECOME UNSTABLE AT LOW PRESSURES AND CAUSE CALIBRATION ERRORS.

All calibration and audit cylinders must be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM). See Chapter 6 of this manual for traceability/certification procedures.

7. Record the initial zero and span potentiometer (pot) settings prior to any adjustments. Analyzer controls will vary with each manufacturer's brand and model. Some analyzers will have only one zero or span pot; while other brands may have zero and span pots for each of the NO, NO₂, and NO_x (NO_y) channels.

Some analyzers are microprocessor controlled and have no potentiometers at all, but they will have readings which correspond to the zero and span pot settings.

Because calibration adjustments will differ between analyzer models, consult the manufacturer's manual before performing the calibration.

8. Use the NO/NO_x (NO_y) Calibration Data sections of the calibration forms (Form 1 & 2) to record the information.
9. Select and record the operating range of the analyzer to be calibrated.

Analyzer Information

Calibrator Information

NO/NO_x Calibration Data

Final Zero Response: NO: _____ NO_x: _____ NO₂: _____

NO₂ GPT Calibration

cal. settings	[NO_x]	[NO]_{orig}	[NO]_{rem}	std conc [NO₂]_{out}	obsv conc [NO₂]_{obsv}	percent diff.
<u>air/gas/O₃</u>	<u>resp/ppm</u>	<u>resp/ppm</u>	<u>resp/ppm</u>	<u>ppm</u>	<u>resp/ppm</u>	
<u>/ /</u>						
<u>/ /</u>						
<u>/ /</u>						
<u>/ /</u>						

NOTE: Select a range for which the analyzer has been designated as an EPA reference method. Most analyzers are calibrated in the 0 to 0.5 ppm range. Refer to the analyzer's manual for designated ranges. The NO_y analyzer can be run at any range that it is capable of and that meets your monitoring needs.

10. Confirm that the analyzer is connected to a recording device such as a data acquisition system (DAS), a strip chart recorder, and/or a digital voltmeter. Since the analyzer will have three output voltage connections (for NO, NO₂, and NO_x (NO_y)), label or be able to differentiate between the three outputs.
11. Adjust the flow of the diluent air (zero air) on the calibrator so that its total output flow exceeds the total demand of the analyzer(s) by at least 25%.

For Example: If the analyzer flow demand is 1.00 liters per minute (L/min), the total output flow from the calibrator should be no less than 1.25 L/min.

The excess flow from the calibrator is necessary to ensure that the analyzer has a sufficient amount of sample. If not, the analyzer could draw air from other than the desired sample stream.

12. Connect the analyzer's "sample in" port to the "sample out" port of the calibrator using a vented nonreactive (TFE Teflon) sample line/manifold. For the NO_y hookup, one line is connected to the converter while a second line bypasses the converter.

NOTE: Logon and annotate all data recording devices (data acquisition system, strip chart recorder, etc.) with the audit starting date, site, parameter, initials, and time.

WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE CALIBRATOR SO THAT EXCESS SAMPLE FLOW CAN BE BLED OFF. FOR THE NO_y CALIBRATION HOOKUP, NO MANIFOLD OR TEE VENT IS USED.

AN UNVENTED SAMPLE GAS COULD PRESSURIZE & DAMAGE THE ANALYZER.

13. Allow the analyzer to sample zero air until NO, NO_x (NO_y), and NO₂ responses have stabilized (usually 10 to 20 minutes). After the responses have stabilized, adjust the analyzer zero control(s) to the desired zero offset. Offsetting the analyzer zero to +1% of scale (i.e. 0.005 ppm on a 0.5 ppm range) is recommended to facilitate observing any negative zero drift. A +5% offset of the data recording device(s) (i.e. strip chart recorder) would also be acceptable.
14. Record the stable zero air analyzer response for NO, NO_x (NO_y), and NO₂ on the calibration form.

15. Attach a stainless steel regulator to the NO gas calibration cylinder. Refer to Section 7.0 for the regulator purge procedure.

NOTE: THE REGULATOR MUST BE PURGED OF ALL AIR BEFORE PROCEEDING WITH THE CALIBRATION (SEE SECTION 7.0 FOR THE REGULATOR PURGE PROCEDURE).

ATMOSPHERIC O₂ IN THE REGULATOR WILL REACT WITH THE NO AND FORM UNWANTED NO₂ IN THE GAS STREAM.

16. Adjust the NO flow from the GPT dilution system (or calibrator) to generate a concentration of approximately 90% of the upper range limit (URL) of the NO channel.

For Example: For an analyzer set on a 0.5 ppm range 90% of the URL would be 0.450 ppm.

17. Calculate the exact NO concentration $[\text{NO}]_{\text{out}}$ using Equation 5-3.

NOTE: BRACKETS [] DENOTE A CONCENTRATION (PARTS PER MILLION, ppm) WHILE AN 'F' WITH A SUBSCRIPT DENOTES A FLOW.

Equation 5-3:

$$[\text{NO}]_{\text{out}} = \frac{F_{\text{NO}} \times [\text{NO}]_{\text{std}}}{F_{\text{NO}} + F_{\text{d}} + F_{\text{o}}}$$

Where:

$[\text{NO}]_{\text{out}}$	=	output concentration of NO in ppm
F_{NO}	=	flow of the NO GPT blending system gas in cc/min
$[\text{NO}]_{\text{std}}$	=	concentration in ppm of the NO gas cylinder
F_{d}	=	flow of the dilution gas (zero air) in cc/min
F_{o}	=	flow through the ozonator

NOTE: MOST MASS FLOW CONTROLLED CALIBRATORS INDICATE THE F_{d} FLOW IN LITERS PER MINUTE (L/min). CONVERT l/min TO cc/min BY MULTIPLYING cc/min x 1000 (cc/min = L/min x 1000).

NOTE: ON MOST CALIBRATORS, THE FLOW THROUGH THE OZONATOR IS FIXED AND ALREADY INCORPORATED INTO THE F_{d} FACTOR. THEREFORE, THE F_{o} CAN BE DROPPED FROM THE EQUATION. CHECK THE CALIBRATOR MANUAL FOR THE EXACT FLOW CONFIGURATIONS.

Example calculation using Equation 5-3:

Assume F_o is already incorporated into the F_d flow,

$$F_{NO} = 45.0 \text{ cc/min}$$

$$F_d = 4,955.0 \text{ cc/min}$$

$$[NO]_{std} = 50.0 \text{ ppm}$$

$$[NO]_{out} = \frac{45.0 \text{ cc/min} \times 50.0 \text{ ppm}}{45.0 \text{ cc/min} + 4,955.0 \text{ cc/min}}$$

$$[NO]_{out} = \frac{2,250.0 \text{ cc/min} \times \text{ppm}}{5,000.0 \text{ cc/min}} = 0.450 \text{ ppm}$$

NOTE: BECAUSE DATA IS REPORTED TO THREE SIGNIFICANT DIGITS, ROUND THE CONCENTRATION TO THE NEAREST THOUSANDS PPM (.XXX).

18. Calculate the exact NO_x (NO_y) concentration $[NO_x]_{out}$ ($[NO_y]_{out}$) using Equation 5-4.

Equation 5-4:

$$[NO_y]_{out} \text{ or } [NO_x]_{out} = \frac{F_{NO} \times ([NO]_{std} + [NO]_{imp})}{F_{NO} + F_d + F_o}$$

Where:

$[NO_2]_{imp}$ = the concentration in ppm of the NO_2 impurity in the NO gas cylinder, $[NO]_{std}$

NOTE: IF $[NO_2]_{IMP} = 0$ OR IS LESS THAN 1% OF THE NO GAS CYLINDER CONCENTRATION, THEN THE $[NO_x]_{OUT}$ CALCULATION IS THE SAME AS THE $[NO]_{OUT}$ CALCULATION.

THE NO_2 IMPURITY IS INDICATED ON THE MANUFACTURER'S LABEL OR CERTIFICATION STICKER ON THE NO GAS CYLINDER $[NO]_{STD}$

19. Record the $[NO]_{out}$ and $[NO_x]_{out}$ ($[NO_y]_{out}$) concentrations on the calibration form.

20. The analyzer should sample the generated concentration until the NO and NO_x (NO_y) responses stabilize (usually 10 to 20 minutes). Adjust the NO (and NO_x (NO_y)) if present) span control to obtain a recorder response as determined by Equation 5-5.

NOTE: IF THE MONITOR RESPONSE EXHIBITS A VERY SLOW RESPONSE TO THE FIRST NO CONCENTRATION, THERE MAY STILL BE SOME RESIDUAL O_2

CONTAMINATION IN THE NO REGULATOR. REPURGE THE REGULATOR (SEE SECTION 7.0).

Equation 5-5:

$$\text{Desired Recorder Response (\% of scale)} = \frac{([\text{NO}]_{\text{out}} \times 100)}{\text{URL}} + Z_{\text{NO}}$$

Where:

URL = upper range limit of the NO channel
Z_{NO} = recorder response of the NO channel

Example calculation using Equation 5-5:

$$\text{Desired Recorder Response (\% of scale)} = \frac{(0.450 \text{ ppm} \times 100)}{0.5 \text{ ppm}} + 5\% = 95.0\%$$

21. After setting the zero and approximately 90% URL NO/NO_x (NO_y) (span) concentrations, determine at least one mid-level concentration between the zero and span concentrations. Run this concentration without any further adjustments to the analyzer.

For example, a typical NO/NO_x (NO_y) calibration with a URL of 0.5 ppm would consist of (listed in order that they should be run):

- a. 0.000 ppm (zero)
- b. 0.400 to .450 ppm (span)
- c. 0.200 to 0.250 ppm (mid-level)

This additional concentration can be generated by either increasing the calibration dilution flow (F_d) or by decreasing the NO cylinder gas flow (F_{NO}). For each concentration generated, calculate the exact NO and NO_x (NO_y) concentrations using Equations 5-3 and 5-4. Record the required information on the NO/NO_x (NO_y) calibration data section on the calibration form.

22. Use a calculator or a linear regression (least squares) computer program to calculate the slope and intercept for the NO channel. Include the upscale calculated concentrations plus the zero to determine the slope and intercept. See Table 2 for example calculations.

OR

23. Adjust the analyzer's NO (and NO_x (NO_y)) span pot(s) or other electronic adjustments so that the slope is a fixed value (i.e., for a 0.5 ppm range: a 0.5 slope for a 1 volt output; a 0.005 slope for a 100 millivolt or strip chart output; a .0005 slope for a 1000 millivolt output).

This method will allow the same slope to be used for data reduction for the entire network. The other calibration concentrations must be within $\pm 2\%$ of the range of the analyzer for

each of the standard concentrations (e.g., if 0.5 ppm range, all measured concentrations must be within .010 ppm of their respective standard concentrations).

24. Use Equation 5-6 to calculate the observed (or measured) concentration for all upscale analyzer responses. Use Equation 5-7 to calculate the difference between the standard and observed concentrations.

The standard concentration is defined as $[\text{NO}]_{\text{out}}$ calculated from Equation 5-3. The observed concentration is defined by the following equation:

Equation 5-6:

$$\text{obsv. response} = (\text{mon. response} - \text{mon. zero response}) \times \text{slope}$$

NOTE: Please make note of the following abbreviations which will be used throughout the rest of this chapter:

a. observed concentration	=	obsv. conc.
b. standard concentration	=	std. conc.
c. monitor response	=	mon. resp.
d. monitor zero response	=	mon. zero resp.
e. percent difference	=	% diff.

NOTE: BECAUSE PRECISION AND ACCURACY DATA IS REPORTED TO THE NEAREST TENTH, THE % DIFF. MAY BE ROUNDED TO THE NEAREST TENTH OF A PERCENT (X.X).

25. All observed concentrations for NO, NO_x (NO_y), and NO₂ channel calibrations must be within the standard concentration by $\pm 2\%$ of the range of the analyzer (.010 ppm).

Table 2
Example Data for Linear Regression

(Y) Concentration [NO] _{out} (ppm)	(X) Monitor Response (volts)	(*) Observed Concentration (ppm)	(**) Observed Concentration (ppm)	(***) Relative Diff.
.450	.907	.450	.450	.000
.326	.654	.323	.324	.002
.205	.427	.209	.210	.005
.124	.262	.126	.128	.004
.000	.007	-.002	.000	.000

* All five points (X & Y) are regressed (Section 5.1.22):

Slope: 0.50267

Intercept: -0.00591

NOTE: Observed concentration is abbreviated as obsv. conc. monitor response is abbreviated as mon. resp.

obsv. conc. = (mon. resp. x slope) + intercept

** Fixed value for the slope (Section 5.1.23):

Slope: 0.500

Zero: 0.007

obsv. conc. = (mon. resp. - zero mon. resp.) x slope

Where:

mon. resp.	=	0.427 v (volt)
mon. zero resp.	=	0.007 v
slope	=	0.500
obsv. conc.	=	(0.427 - 0.007) x 0.500
obsv. conc.	=	0.210 ppm

Equation 5-7:

$$\% \text{ diff.} = \frac{\text{obsv. conc.} - \text{std. conc.}}{\text{std. conc.}} \times 100$$

Where:

std. conc. = 0.205 ppm

obsv. conc. = 0.210 ppm

Example calculation:

diff. = 0.210 - 0.205 ppm

diff. = 0.005 ppm

Analyzers which cannot routinely meet the calibration limit (.010 ppm) may be in need of maintenance.

26. Repeat steps 22 to 25 of Section 5.1 for the NO_x (NO_y) channel calculations.

27. Be sure to record all information/data on the GPT Calibration Form (Form 1 or 2).

28. Perform and then record any analyzer diagnostic test results. These tests provide baseline data for future troubleshooting.

29. The NO₂ channel is now ready for calibration.

5.2 NO₂ Calibration Procedure for NO/NO₂/NO_x or NO/NO₂/NO_y Analyzer

After calibrating the NO and NO_x (NO_y) channels, the NO₂ channel is calibrated using the Gas Phase Titration (GPT) technique. Ozone (O₃) is used to titrate against an excess amount of NO gas in order to produce NO₂ concentrations.

The NO₂ channel calibration procedure is as follows:

1. Rerun the zero air and record the analyzer response for the NO, NO_x (NO_y), and NO₂ channels.
2. Adjust the NO flow from the GPT blending system (calibrator) to generate a concentration of approximately 90% of the URL of the NO channel (See 16 to 18 of Section 5.1 for the exact procedures and calculations).
3. After the analyzer has stabilized, record the channel responses as [NO]_{orig} and [NO_x] ([NO_y]) on the NO₂ section of the calibration form. Convert the responses to ppm concentrations

using the slope and analyzer zero response for each respective NO and NO_x (NO_y) channel.

[NO]_{orig} (original NO) is defined as the concentration of NO before the titration with O₃.

Example calculation:

	<u>Slope</u>	<u>Zero Response</u>	<u>Monitor Response</u> *
NO	0.500	0.007 v	0.897 v
NO _x (NO _y)	0.500	0.007 v	0.899 v

* assume a 0 to 1.0 volt dc analyzer output range

Using Equation 5-6:

$$[\text{NO}]_{\text{orig}} = (0.897 \text{ v} - 0.007 \text{ v}) \times 0.500 = 0.445 \text{ ppm}$$

$$[\text{NO}_x]_{\text{orig}} ([\text{NO}_y]_{\text{orig}}) = (0.899 \text{ v} - 0.007 \text{ v}) \times 0.500 = 0.466 \text{ ppm}$$

4. Adjust the O₃ generator on the calibrator to produce an NO₂ analyzer response of approximately 80% of scale.

To prevent calibration errors, be sure to allow at least .050 ppm of NO to remain ([NO]_{rem}).

Example calculation:

80% of a 0.5 ppm range = 0.400 ppm

NOTE: It is helpful during the titration to have each of the analyzer's three outputs (NO, NO₂, NO_x (NO_y)) connected to a strip chart recorder. When the calibrator's ozone generator is turned on, the analyzer will respond as follows: the NO response will decrease; the NO₂ response will increase; the NO_x (NO_y) response will not change or the response may decrease slightly.

5. After the analyzer's responses have stabilized (usually 15 to 25 minutes) record the analyzer responses for [NO]_{rem}, [NO_x]([NO_y]), and [NO₂]_{meas} in mv, v, or % chart. Refer to the NO₂ section of the calibration form, Form 1 or 2.

[NO]_{rem} (remaining NO) is defined as the concentration of remaining NO after titration with O₃.

[NO₂]_{meas} (measured or observed NO₂) is defined as the concentration calculated from the analyzer's response for the NO₂ channel.

6. Calculate the concentration of NO₂ produced which is indicated as [NO₂]_{out} by using Equation 5-8.

NOTE: The $[\text{NO}_2]_{\text{out}}$ is also called the standard NO_2 concentration.

Equation 5-8:

$$[\text{NO}_2]_{\text{out}} = [\text{NO}]_{\text{orig}} - [\text{NO}]_{\text{rem}}$$

Where:

$$\begin{aligned} [\text{NO}]_{\text{orig}} &= 0.445 \text{ ppm} \\ [\text{NO}]_{\text{rem}} &= 0.051 \text{ ppm} \end{aligned}$$

Example calculation:

$$[\text{NO}_2]_{\text{out}} = 0.445 \text{ ppm} - 0.080 \text{ ppm} = 0.365 \text{ ppm}$$

7. One of the steps to be followed next will depend on the brand and model of the analyzer.
 - a. For an analyzer with a NO_2 span pot., adjust the span pot. until the analyzer's output corresponds to the calculated $[\text{NO}_2]_{\text{out}}$ concentration. Always refer to the analyzer's manual for specific instructions.
 - b. For a microprocessor controlled analyzer (i.e., TECO 42), refer to the manual and adjust the NO_2 output until it agrees with the calculated $[\text{NO}_2]_{\text{out}}$ concentration.
 - c. For an analyzer without an NO_2 span potentiometer (pot) (i.e., CSI 1600), record the analyzer's output for the NO_2 channel. Since no adjustment can be made to this channel it is extremely important to have first accurately calibrated the NO and NO_x channels.
8. Titrate at least one additional NO_2 concentration, $[\text{NO}_2]_{\text{out}}$, by changing the ozonator output on the GPT blending system (calibrator). For each concentration calculate and record the following:
 - a. Analyzer response for the NO channel and calculated $[\text{NO}]_{\text{rem}}$ concentration
 - b. Analyzer response for the NO_x (NO_y) channel and the calculated $[\text{NO}_x]([\text{NO}_y])$ concentration
 - c. Analyzer response for the NO_2 channel and the calculated $[\text{NO}_2]_{\text{out}}$ concentration

A typical NO_2 calibration will have points in the following ranges:

1. .0 ppm (zero)
2. 0.280 to 0.320 ppm recommended
3. 0.080 to .120 ppm recommended

9. Use a calculator or a computer with a linear regression (least squares) program in order to calculate the slope and intercept for the NO₂ channel. Include the four upscale NO₂ concentrations, [NO₂]_{out}, plus the monitor response for zero air in the linear regression. See Table 2 for an example calibration.

OR

10. Adjust the analyzer's NO₂ span potentiometer (pot) so that the slope is a fixed value (i.e. for a 0.5 ppm range: a 0.5 slope for a 1 volt output; a 0.005 slope for a 100 millivolt or strip chart output; a 0.0005 slope for a 1000 millivolt output).

For analyzers with no NO₂ adjustment, assume a constant slope
(See (**) Table 2).

11. For all NO₂ upscale points, calculate the observed concentration, [NO₂]_{meas}, and the percent difference between the standard, [NO₂]_{out}, and the observed, [NO₂]_{meas}. Use Equations 5-6 and 5-7.
12. All observed concentrations for NO₂ must be within the corresponding standard concentrations by $\pm 2\%$ of the analyzer range. If any observed concentration is found to be greater than $\pm 2\%$ of the analyzer range, then recalculate and/or rerun that concentration.

NOTE: If the percent difference is greater than $\pm 2\%$, the NO and/or the NO_x channels may have drifted. If this is the case then the entire calibration, starting with the NO/NO_x calibration, may have to be repeated.

13. The Code of Federal Regulations requires that all NO/NO₂/NO_x analyzers have a converter efficiency of at least 96%. Data from analyzers with a converter efficiency of less than 96% is considered invalid.

Converter efficiency is defined as the percent of NO₂ which is converted to NO so that the NO_x (NO_y) component can be measured by the analyzer.

See Figure 1 for an analyzer diagram. Inefficient converters ($< 96\%$) do not convert all of the NO₂ to NO which results in a NO_x (NO_y) concentration biased low.

If the converter efficiency falls below 96%, then the converter must be replaced. The analyzer must then be recalibrated.

For most analyzers, converter efficiency must be calculated at the time of each calibration. Section 6.1 outlines this procedure.

For microprocessor controlled analyzers (i.e. TECO 42), the converter efficiency is automatically calculated. The procedures of Section 6.0 would then not have to be followed for the TECO 42.

Check the analyzer's manual to determine if the converter efficiency has to be manually calculated.

14. After finishing an on-site calibration, complete the following steps:

- a. Reconnect the analyzer to the sample manifold.
- b. Ensure that the analyzer is in the monitor mode.
- c. Ensure that the analyzer is connected to all data recording devices and that all strip charts have been annotated.

NOTE: All strip charts should be annotated with the following information: site name, date, chart speed, calibration starting time, initials of the person performing the calibration, label all responses with the applicable standard concentrations and the parameter, label the initial and final zero, and the calibration ending time.

In addition, record and post the following:

- d. Record all pertinent information in the site logbook.
- e. Post a copy of the calibration at the site.

NOTE: Residual NO and NO₂ trapped in a calibrator can cause stability problems during the next calibration. Purge the calibrator with zero air after each calibration is completed.

6.0 Converter Efficiency Calculations

The converter efficiency is calculated from data generated from the upscale concentrations titrated during the NO₂ part of the analyzer calibration. (See Equation 5-9).

Equation 5-9:

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

OR

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_y]_{\text{orig}} - [\text{NO}_y]_{\text{rem}})$$

Where:

- | | | |
|------------------------------------|---|--|
| $[\text{NO}_2]_{\text{converted}}$ | = | the concentration (ppm) of NO ₂ converted by the analyzer's catalytic converter |
| $[\text{NO}_2]_{\text{out}}$ | = | the standard concentration (ppm) of NO ₂ produced by the GPT blending system |
| $[\text{NO}_x]_{\text{orig}}$ | = | the concentration (ppm) of NO _x (original) before titration |
| $[\text{NO}_x]_{\text{rem}}$ | = | the concentration (ppm) of NO _x (remaining) concentration after titration |

$[\text{NO}_y]_{\text{orig}}$ = the concentration (ppm) of NO_y (original) before titration
 $[\text{NO}_y]_{\text{rem}}$ = the concentration (ppm) of NO_y (remaining) concentration after titration

Example calculation: See Figure 2 for an example calculation for $\text{NO}/\text{NO}_2/\text{NO}_x$.

The required data for a converter efficiency calculation are: the $[\text{NO}_x]_{\text{orig}}$ ($[\text{NO}_y]_{\text{orig}}$) concentration (prior to O_3 titration), the $[\text{NO}_x]_{\text{rem}}$ ($[\text{NO}_y]$) concentrations (after O_3 titration) and the $[\text{NO}_2]_{\text{out}}$ concentrations. See Forms 1 and 2 for the GPT calibration and Forms 4 and 5 for an example converter efficiency calculation.

6.1 Calculation Procedure for Converter Efficiency

1. Transfer the concentrations of $[\text{NO}_2]_{\text{out}}$, $[\text{NO}_x]_{\text{orig}}$ ($[\text{NO}_y]_{\text{orig}}$), and $[\text{NO}_x]$ ($[\text{NO}_y]$) from the NO_2 GPT data table (Form 1) to the Converter Efficiency data table (Form 3). Also include zero points ($[\text{NO}_2]_{\text{out}} = 0$ and $[\text{NO}_2]_{\text{conv}} = 0$) in the data table. For NO_y , the concentrations will be transferred from Form 2 to Form 4.
2. Using a calculator or a computer with a linear regression (least squares) program, enter the $[\text{NO}_2]_{\text{out}}$ on the x-axis and the $[\text{NO}_2]_{\text{conv}}$ on the y-axis.
3. Use the upscale data sets plus the zero value to determine a slope.
4. Percent converter efficiency is defined by Equation 5-10.

Equation 5-10:

$$\text{Percent Converter Efficiency} = \text{Slope} \times 100$$

5. Converter efficiency must be 96% or greater. Since this efficiency is derived from several calculated data points, it is possible for the efficiency to be greater than 100%.

Form 3
Converter Efficiency NO/NO₂/NO_x

Point	(X) [NO₂]_{out} (ppm)	[NO_x]_{orig} (ppm)	[NO_x]_{rem} (ppm)	(Y) [NO₂]_{conv} (ppm)
1				
2				
3				
4				
5				

$$[\text{NO}_2]_{\text{conv}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

$$\text{Converter Efficiency} = \text{Slope} \times 100$$

Slope: _____

Converter Efficiency: _____%

Comments: _____

Form 4
Converter Efficiency NO/NO₂/NO_y

Point	(X) [NO ₂] _{out} (ppm)	[NO _y] _{orig} (ppm)	[NO _y] _{rem} (ppm)	(Y) [NO ₂] _{conv} (ppm)
1				
2				
3				
4				
5				

$$[\text{NO}_2]_{\text{conv}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_y]_{\text{orig}} - [\text{NO}_y]_{\text{rem}})$$

$$\text{Converter Efficiency} = \text{Slope} \times 100$$

Slope: _____

Converter Efficiency: _____%

Comments:

Figure 2
Converter Efficiency

Point	(X) [NO ₂] _{out} (ppm)	[NO _x] _{orig} (ppm)	[NO _x] _{rem} (ppm)	(Y) [NO ₂] _{conv} (ppm)
1	0.000	0.451	0.451	0.000
2	0.398	0.451	0.451	0.398
3	0.298	0.451	0.451	0.298
4	0.199	0.451	0.453	0.201
5	0.101	0.451	0.452	0.102

$$[\text{NO}_2]_{\text{conv}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

$$\text{Converter Efficiency} = \text{Slope} \times 100$$

Slope: .99900

Converter Efficiency: 99.9%

Comments: Diagnostic tests were performed before and after the calibration with the following results:

Test	Initial	Final	Unit
Time Constant	60	60	sec
Cooler Temperature	-3.7	-3.7	°C
Converter Temperature	329	329	°C
Reaction Chamber Temp.	49.8	49.9	°C
NO Zero Background	5.7	6.2	
NO _x Zero Background	6.6	8.5	
Analog Offset %	0.0	0.0	
Dip #1 to #8 status	2,3,6	2,3,6	on
T Program	4205tP	4205tP	
Internal Temperature	31.9	36.8	°C

7.0 Regulator Purge Procedure

NO gas is very reactive with atmospheric oxygen. NO will react with oxygen in air to form unwanted NO₂ in the regulator and gas delivery line. Therefore, it is necessary to purge and evacuate the regulator and gas delivery line of air in order to avoid this NO₂ formation.

The regulator and gas delivery line can be evacuated of air by using an electric pump or a hand operated vacuum pump. The procedure is as follows:

1. Attach a stainless steel regulator (CGA 660 fitting) to the NO gas cylinder.

A single or dual stage regulator can be used. The regulator should be equipped with an output shutoff valve made of a nonreactive material.

Attach the gas delivery line to the regulator (attach to the output shutoff valve). An 1/8" outside diameter (1/8" OD) Teflon gas delivery line is recommended.

A male quick connect type shutoff fitting should be attached to the end of the gas delivery line. This fitting will allow the vacuum to be maintained in the gas delivery line.

2. Attach the vacuum pump (equipped with a female quick connect type fitting) to the gas delivery line. Evacuate the regulator and gas delivery line of air with the vacuum pump (hand vacuum or electric pump).
3. Disconnect the vacuum pump and then open the cylinder valve to fill the regulator and gas delivery line with NO.
4. Close the cylinder shutoff valve and reconnect the vacuum pump to the gas delivery line. Immediately start the evacuation of the regulator and gas delivery line.

If an electric pump is used, evacuate for at least 15 seconds. If a hand vacuum pump is used, draw as much of a vacuum as the hand vacuum will allow.

5. Repeat steps 3 and 4 of 7.0 at least 3 times. It is important to evacuate as much air as possible from the regulator and lines. Flushing the system several times will minimize problems with the calibration.
6. If the analyzer responds slowly to the first upscale NO concentration or the analyzer's NO₂ channel is indicating an upscale concentration of NO₂, the regulator purge procedure should be repeated.

8.0 Quality Assurance Audits

Quality assurance audits are performed to ensure the validity of the data submitted to the National AQS Data Bank. Results of these audits are also used to estimate the Precision and Accuracy (P&A) of the monitoring network's data. Reports of the P&A statewide are submitted quarterly by IDEM/OAQ/QAS to the USEPA. See Chapter 13, Quality Assessment and Statistical Analysis of Air Monitoring Data, of this manual for detailed information on P&A.

8.1 Data Validation and Precision Audits

Routine audits are performed every two weeks (biweekly) in order to assess the validity and precision of the NO₂ data. The biweekly audit consists of running two upscale NO₂ concentrations from a GPT blending system (audit device) with a certified NO standard gas cylinder. The audit device must meet the same criteria as that of the GPT blending system used for the calibration (Section 4.2). The audit device must be certified by the IDEM-QAS (Section 4.2 and Chapter 6).

The first biweekly audit point consists of an NO₂ concentration of approximately 80% URL (0.350 ppm to 0.420 ppm). This concentration is used to validate data back to the most recent audit or calibration. See Chapter 11, Valid Data Requirements, in this manual for the details of data validation.

The second biweekly audit point consists of an NO₂ concentration in the required range of 0.08 ppm to 0.10 ppm. This second audit point is used to assess the precision of the data based on a quarterly calculation.

The same GPT blending system used to calibrate the analyzer may be used to perform the biweekly audit on the analyzer. It is suggested (but not required) that the auditor be different from the person who performed the calibration.

Table 3 shows the required ranges for NO₂ precision and accuracy audit concentrations.

Record all information below on the NO₂ audit form or equivalent. See Form 5.

NOTE: MAKE NO ADJUSTMENTS TO THE ANALYZER PRIOR TO THE AUDIT.

Form 5
NO_x Audit Form

Site _____ Auditor _____ Date _____
Last Audit _____ Temp _____ °C
Audit Start Time _____ Audit End Time _____
Analyzer Brand/Model/SN _____
Cal. Date _____ Range _____
TECO: C.E. _____ S.F. _____ B.F. _____ VAC: _____

Primary Recorder/Range _____ Secondary Recorder/Range _____
DVM/Range _____

Audit Std. Brand/Model/SN _____ Cert Date _____
Flow Meter Cert. Date _____ Cyl. SN _____ Cyl. Conc. _____ Cyl. PSI _____

Zero Response(s) NO₂ Prim _____ Sec _____ DVM _____
NO Prim _____ DVM _____ NO_x Prim _____ DVM _____

Validation Point Std. NO Conc. _____
Response(s) NO Prim _____ DVM _____ Meas. NO Conc. _____ NO % Diff _____
NO_x Prim _____ DVM _____ Meas. NO_x Conc. _____ NO_x % Diff _____

O₃ Setting _____ NO₂ GPT Response Prim. _____ Sec. _____ DVM _____
NO GPT Remaining Prim _____ DVM _____ Conc.(.08-.12) _____
Meas. NO₂ Conc. _____ Std. NO₂ Conc. (.35-.45) _____ NO₂ % Diff _____

Precision Point Std. NO Conc. _____
Response(s) NO Prim _____ DVM _____ Meas NO Conc. _____ NO %
Diff _____
NO_x Prim. _____ DVM _____ Meas NO_x Conc. _____ NO_x % Diff _____

O₃ Setting _____ NO₂ GPT Response Prim. _____ Sec. _____ DVM _____
NO GPT Remaining Prim. _____ DVM _____ Conc.(.08-.12) _____
Meas NO₂ Conc. _____ Std. NO₂ Conc.(.08-.10) _____ NO₂ % Diff _____

Remarks: _____

The field audit procedure is as follows:

1. Record the station name and the AQS site identification number on the NO₂ audit form.
2. Identify the person performing the audit (initials), and record the audit date.
3. Record the analyzer's operational period (date and time). The operational period is defined as the period of time starting from the last audit or calibration (date and time) to the current audit (date and time).
4. Record the analyzer's manufacturer name, model number, and serial number.
5. Record the analyzer's settings: range, flows, vacuum, etc.

NOTE: It is a good idea to inspect the analyzer before the start of the field audit. For example: Check to see that the analyzer is in the monitor mode; the sample line is connected to the sample manifold or outside sample line; the analyzer is connected to the data recording device(s); and if there are any other conditions that could affect the data or the field audit results.

6. Record the analyzer's last calibration date. Analyzers must be calibrated at least every six months.
7. Record the audit device manufacturer name, model number, and serial number.
8. Record the NO audit gas cylinder number, certified concentration, and certification date.

NOTE: DO NOT USE CYLINDERS WITH PRESSURES < 200 PSIG.

GASES MAY BECOME UNSTABLE AT LOW PRESSURES AND CAUSE AUDIT ERRORS.

BE SURE THAT THE AUDIT GPT BLENDER AND GAS HAVE A CURRENT CERTIFICATION (WITHIN THE LAST 6 MONTHS) BEFORE PROCEEDING.

9. Record the zero and span potentiometer (pot) settings. Analyzer controls will vary with each manufacturer's brand and model. Some analyzers will have only one zero or span potentiometer (pot) while other brands may have zero and span potentiometers (pots) for each of the NO, NO₂, and NO_x (NO_y) channels. Microprocessor controlled analyzers have no potentiometers but will have readings which correspond to the zero and span pot settings.
10. Indicate the analyzer's primary and secondary recording device. If a digital voltmeter (DVM) is to be used during the audit then indicate this on the audit form.

11. Confirm that the analyzer is connected to a recording device such as: a data acquisition system (DAS), a strip chart recorder, and/or a digital voltmeter. Since the analyzer will have three output voltage connections (for NO, NO₂, and NO_x (NO_y)), label or be able to differentiate between the three outputs.
12. Adjust the flow of the diluent air (zero air) on the audit device so that its total output flow exceeds the total demand of the analyzer by at least 25%.

See Section 5.1 for example calculations.

13. Connect the analyzer's "sample in" port to the "sample out" port of the audit device using a vented nonreactive (TFE Teflon) sample line/manifold. For the NO_y hookup, one line goes to the converter while one bypasses the converter.

NOTE: Logon and annotate all data recording devices (data acquisition system, strip chart recorder, etc.) with the audit starting date, site, parameter, initials, and time.

WARNING: THE SAMPLE GAS MUST BE DELIVERED TO THE ANALYZER AT ATMOSPHERIC PRESSURE. A MANIFOLD OR TEE VENT MUST BE USED FROM THE AUDIT DEVICE SO THAT EXCESS SAMPLE FLOW CAN BE BLED OFF. AN UNVENTED SAMPLE GAS COULD PRESSURIZE & DAMAGE THE ANALYZER. FOR THE NO_y AUDIT HOOKUP, NO MANIFOLD OR TEE VENT IS USED.

14. Allow the analyzer to sample zero air until NO, NO₂, and NO_x, and responses stabilize (usually 10 to 20 minutes). Record the analyzer responses to zero air on the audit form.
15. Attach a stainless steel regulator to the NO audit cylinder. Refer to Section 7.0 for the regulator purge procedure.

NOTE: THE REGULATOR MUST BE PURGED OF ALL AIR BEFORE PROCEEDING WITH THE AUDIT. ATMOSPHERIC O₂ IN THE REGULATOR WILL REACT WITH THE NO AND FORM UNWANTED NO₂ IN THE GAS STREAM.

16. For the data validation concentration, adjust the NO flow from the audit GPT blending system to generate a concentration of approximately 90% of the upper range limit (URL) of the NO channel. An NO concentration in the .430 ppm to .470 ppm range is suggested.
17. Calculate the exact NO concentration [NO]_{out} using Equation 5-3. Record this concentration under Std. NO Conc. on the audit form. Also record the audit setting, gas flow, and total flow.

See Section 5.1 for Equation 5-3 and example calculations.

18. After the analyzer responses have stabilized, record the responses as Response NO, Primary/DVM and Response NO_x (NO_y), Primary/DVM on the audit form.
19. Using the analyzer's respective NO/NO_x (NO_y) current calibration slopes and zero responses with Equation 5-6, convert the Response NO, Primary and Response NO_x, Primary to concentrations (ppm).

Record the respective concentrations as Meas. NO Conc. and Meas. NO_x Conc.

See Section 5.1 for Equation 5-6 and example calculations.

NOTE: The standard concentration (NO Std. Conc.) is defined as [NO]_{out} calculated from Equation 5-3. The observed concentration (obsv. conc. or meas. conc.) is defined by Equation 5-6.

NOTE: IF THE MONITOR RESPONSE EXHIBITS A VERY SLOW RESPONSE TO THE FIRST NO CONCENTRATION, THERE MAY STILL BE SOME RESIDUAL O₂ CONTAMINATION IN THE NO REGULATOR. REPURGE THE REGULATOR, SEE SECTION 7.0.

20. Calculate and record the percent difference (% diff.) between the standard concentration (Std. Conc.) and observed concentration (Meas. Conc.) for the NO and NO_x (NO_y) channels. See Equation 5-7 for the % diff. calculation.
21. The results of the NO and NO_x (NO_y) channel audits will determine one of following three outcomes:
 - a. If the percent difference for the NO or NO_x (NO_y) channel is greater than $\pm 15\%$, the audit may be ended; however, additional points may be of value to determine what is going on with the equipment. The data from the last audit or calibration to the present is invalid. The analyzer must be recalibrated before data will again be valid.
 - b. If the percent difference for the NO or NO_x (NO_y) channel is greater than $\pm 7.5\%$, then inform the operator that the analyzer is out of calibration. The data is considered valid but a recalibration must be done as soon as possible. The rest of the NO₂ channel audit can still proceed (Section 8.1, Step 22).
 - c. If the percent difference for the NO or NO_x (NO_y) channel is less than $\pm 7.5\%$, then the analyzer is in calibration and the audit can proceed (Section 8.1, Step 22).
22. For the NO₂ data validation concentration, adjust the O₃ generator on the audit GPT blending system to produce a NO remaining [NO]_{rem} in the 0.08 to 0.12 ppm range.

An NO₂ analyzer response of approximately 80% of the URL should be produced.

NOTE: THE CODE OF FEDERAL REGULATIONS (40 CFR 58 APPENDIX A) REQUIRES A RESIDUAL NO CONCENTRATION, [NO]_{REM}, DURING THE TITRATION OF ALL NO₂ AUDIT CONCENTRATIONS. THIS RESIDUAL MUST BE IN THE RANGE OF 0.08 ppm TO 0.12 ppm.

23. After the analyzer responses have stabilized, record the NO REMAINING and NO₂ RESPONSE readings from the primary, secondary, and DVM recording devices. Also, record the O₃ SETTING on the audit device.
24. Calculate and record the standard NO₂ concentration [NO₂]_{STD} using Equation 5-10.

Equation 5-10:

$$[\text{NO}_2]_{\text{std}} = \frac{(\text{NO}_{\text{orig}} \text{ response} - \text{NO}_{\text{rem}} \text{ response}) \times [\text{NO}]_{\text{orig}}}{\text{NO}_{\text{orig}} \text{ response} - \text{NO zero response}}$$

Where:

NO_{orig} = the monitor response in % chart, millivolts or volts before O₃ titration
 NO_{rem} = the monitor response in % chart, millivolts or volts after O₃ titration
 [NO]_{orig} = the original NO concentration (ppm) before O₃ titration

Example calculation using Equation 5-10:

Where:

NO_{orig} = 0.947 volt
 NO_{rem} = 0.171 volt
 NO zero response = 0.007 volt
 [NO]_{orig} = 0.472 ppm
 [NO₂]_{std} = $\frac{(0.947 \text{ volt} - 0.171 \text{ volt}) \times 0.472 \text{ ppm}}{0.947 \text{ volt} - 0.007 \text{ volt}}$
 [NO₂]_{std} = $\frac{0.776 \text{ volt} \times 0.472 \text{ ppm}}{0.940 \text{ volt}} = 0.390 \text{ ppm}$

25. Calculate the observed or measured concentration (obsv. conc./meas. conc.) of NO₂ and the analyzer's current slope for the NO₂ channel. Use Equation 5-6 (Page 17). Record the analyzer's NO₂ response and the analyzer's NO₂ zero response on form 5. See form 5 (Page 30).

Example calculation:

Where:

NO₂ response = 0.776 volt
 NO₂ zero response = 0.006 volt

$$\begin{aligned}\text{NO}_2 \text{ calibration slope} &= 0.5 \\ \text{obsv. conc.} &= (0.776 \text{ volt} - 0.006 \text{ volt}) \times 0.5 \\ \text{obsv. conc.} &= 0.770 \text{ volt} \times 0.5 = 0.385 \text{ ppm}\end{aligned}$$

26. Calculate and record the percent difference (% diff.) between the [NO₂] observed concentration (obsv. conc.) and the [NO₂] standard concentration (std. conc.). Use Equation 5-7 on page 42.

NOTE: BECAUSE P&A DATA IS REPORTED TO THE NEAREST TENTH OF A PERCENT, THE % DIFF. SHOULD BE ROUNDED TO THE NEAREST TENTH OF A PERCENT (X.X).

27. The results of the NO₂ channel audit will determine one of the following outcomes:

- a. If the percent difference for the NO₂ channel is greater than $\pm 15\%$, then the audit may be ended; however, additional points may be of value to determine what is going on with the equipment. The data from the last audit or calibration is invalid. The analyzer must be recalibrated before data will again be valid.
- b. If the percent difference for the NO₂ channel is greater than $\pm 7.5\%$, then inform the operator that the analyzer is out of calibration. The data is considered valid but a recalibration must be done as soon as possible. The rest of the NO₂ channel audit can still proceed (Section 8.1, Step 28).
- c. If the percent difference for the NO₂ channel is less than $\pm 7.5\%$, there are no problems and the audit can proceed (Section 8.1, Step 28).

28. For the NO₂ precision point, adjust NO flow on the audit GPT blending system to obtain an NO concentration ([NO]_{orig}) in the range of 0.17 ppm to 0.20 ppm. This NO concentration will allow the titration of an NO₂ concentration in the 0.08 ppm to 0.10 ppm range.

See Table 4 for a list of NO and NO₂ titration ranges on page 37.

See Section 5.1 for NO flow equations and calculation examples.

Remember, during titration a residual of 0.08 to 0.12 ppm of NO is required.

Before performing a field audit with a particular audit GPT blending system, it is a good idea (and time saver) to know the general flow and ozonator settings for each audit concentration.

29. After the NO response has stabilized, titrate an NO₂ concentration in the 0.08 ppm to 0.10 ppm range.

Repeat steps in Section 8.1, Steps 23 to 26 to complete the audit.

30. After the audit has been completed (biweekly or accuracy), perform the following:

- a. Reconnect the analyzer's sample line to the outside sample line or manifold.
- b. Ensure that the analyzer is in the monitor mode and has its normal flow.
- c. Ensure that the data recording devices are connected to the analyzer and are registering a signal.
- d. Logoff and annotate all data recording devices with the ending time of the audit, the initials of the auditor, and the results of the audit (% diff.).
- e. For a strip chart recorder be sure to indicate on the chart: site name, audit starting and ending date/time, zero response, upscale responses for standard concentrations, the parameter, and the auditor's initials.
- f. Record all applicable information in the site logbook: include at least the audit date, the initials of the auditor, the type of audit (validation/precision and/or accuracy), and the results of the audit (% diff.).

NOTE: Residual NO and NO₂ trapped in a calibrator can cause stability problems during the next audit. It is a good idea to purge the audit device with zero air for a few minutes after each audit is completed.

8.2 Accuracy Audits

Accuracy audits must be performed on at least 25% of the network's analyzers each calendar quarter. At the end of the year, all analyzers must have had an accuracy audit. Networks which have 4 or fewer analyzers must conduct accuracy audits so that all analyzers have had an accuracy audit by the end of the year. Accuracy would then be calculated in the 2nd and 4th quarters of the year. Since this is a statistical assessment of the data's accuracy, it is suggested that accuracy audits be conducted more often than once per quarter (i.e., monthly). This ensures a larger and more representative database for the accuracy calculations.

Only NO₂, a criteria pollutant, must have accuracy audits. The NO and NO_x (NO_y) channels do not require accuracy audits.

The Federal Register requires that a different audit GPT blender and gas standard from that of the calibrator used for the calibration be used to perform the accuracy audit. The auditor should also be different from that of the person who performed the calibration.

The analyzer must be collecting valid data on all channels (NO, NO₂, or NO_x (NO_y) channels $\leq \pm 15\%$ for the Level 1 data validation concentration) in order to conduct an accuracy audit.

Table 3
Required (Code of Federal Regulations) Concentrations for Precision and Accuracy

Level	NO ₂ Accuracy Audit Concentrations (ppm)
1	0.03 to 0.08
2	0.15 to 0.20
3	0.35 to 0.45

NO₂ precision range: 0.08 to 0.10 ppm

Table 4
Suggested Accuracy Audit NO and NO₂ Titration Concentrations

NO Range (ppm)	NO ₂ Range (ppm)
0.43 to 0.47	0.38 to 0.42
0.27 to 0.32	0.15 to 0.20
0.17 to 0.20	0.08 to 0.10

NOTE: IF ANY CHANNEL (NO, NO_x (NO_y) OR NO₂) HAS A DATA VALIDATION % DIFF. > 15%, DO NOT CONDUCT THE ACCURACY AUDIT.

Refer to Table 4 for suggested NO concentrations for titration.

Follow steps 1 to 26 and 30 of Section 8.1 for the accuracy audit.

9.0 Data Reduction and Reporting

The primary/secondary National Ambient Air Quality Standard (NAAQS) for NO₂ is an annual arithmetic mean of 0.053 ppm.

The continuous data produced for entry into the National Air Quality System (AQS) data bank must be reduced to 24 1-hour averages per day. This reduction must follow the guidelines and requirements set forth in Chapter 12 of this manual.

Although not specified as criteria pollutants, NO and NO_x (NO_y) data should also be submitted to IDEM. NO and NO_x (NO_y) data may be validated through biweekly audits but precision and accuracy audits are not required for this data.

Data should be submitted to the IDEM Ambient Monitoring Section within 60 days after the end of the quarter. This will allow sufficient time for review before AQS submittal deadlines of 90 days after the end of each reporting calendar quarter.

10.0 Routine Station Operation

Essential to a good quality assurance program are scheduled checks for verifying the operation of the monitoring system. At least once per week, an operator should visit each site in order to evaluate operating conditions and to perform routine maintenance.

Conducting routine site/analyzer checks and taking prompt corrective actions for any problems will minimize the loss of data. The results of any of the checks below can directly affect the validity of the data.

10.1 Station Checks

All sites should have a bound logbook in which site checks, analyzer maintenance/checks, and audit information can be recorded.

1. The average shelter temperature should range from 20 °C to 30 °C (68 °F to 86 °F). A certified thermograph or other temperature recording device must be installed to continuously monitor the site temperature fluctuations as per 40 CFR Part 53.31(1).

Data may be invalidated by the IDEM-QAS any time the shelter temperature is out of the 15 °C to 33 °C (59.0 °F to 91.4 °F) range.

2. The sample manifold/blower or lines should be inspected weekly for cleanliness, leaks, and obstructions.
3. The exterior sample line, candy cane, and funnel should be inspected weekly for cleanliness, breaks, and obstructions.
4. All data recording devices should be inspected for ink trace or printout legibility, paper supply, and correct time (or time synchronization).

For those counties in Indiana which change time in the spring and in the fall, do not change the time on the data recording devices. **All data recording devices remain on the same time year-round (standard time).**

5. Record all station activities/checks in the site logbook.

10.2 Analyzer Checks

1. All analyzers must be equipped with an inlet particulate filter assembly. Check the analyzer's manual for the recommended filter pore size. Usually a 5 micron pore size, 47 millimeter diameter, nonreactive round filter is used.

The inlet particulate filter must be changed at least weekly. A clean filter will minimize the reaction and loss of the NO₂ in the sample air with particulate matter on the filter.

After installing a clean filter, be sure to tightly reassemble the inlet filter holder in order to prevent leaks.

2. NO/NO₂/NO_x or NO/NO₂/NO_y analyzers use desiccant columns for the drying of the air drawn into the analyzer's ozonator.

Two desiccant columns connected in series must be used on each analyzer. An indicating (color change) type desiccant is used in the columns. This indicating desiccant can consist of either silica gel or anhydrous CaSO₄ (drierite).

The desiccant columns should be inspected weekly for any color change. The first column (farthest from the analyzer) should be changed whenever the desiccant has changed color (color change indicates that the column is no longer removing moisture).

Humid conditions, especially in the summer months, will require more frequent changing of the columns.

NOTE: ALWAYS USE TWO COLUMNS IN SERIES AND NEVER LET THE INNER COLUMN BECOME EXPENDED.

EXPENDED DRYER COLUMNS WILL CAUSE THE ANALYZER TO BE OUT OF CALIBRATION.

EXPENDED DRYER COLUMNS CAN CAUSE AS MUCH AS A 25% CALIBRATION ERROR, RESULTING IN LOW NO₂ VALUES.

3. Check weekly and record, in the site log, analyzer flow rates and vacuum readings. Readings should correspond to those from the last calibration.
4. Check weekly and record, in the site log, the zero and span potentiometer (pot) settings. Readings should correspond to those from the last calibration.
5. Verify that the analyzer is in the monitor mode and that it is connected to and providing a signal to the primary and secondary data recording devices.
6. Some analyzer models have extensive diagnostic tests and some of these tests may need to be conducted weekly. Check the site logbook and conduct any indicated tests.
7. Routine maintenance must also be performed on all analyzers. Consult the analyzer's equipment manual for specific requirements and frequencies that indicate what maintenance must be performed and how often. A schedule of routine maintenance should be made and followed. Some maintenance items common to most analyzers are:
 - a. sample pump
 - b. catalytic converter

- c. interior filters/screens (cleaning or replacement)
- d. cooling fan (cleaning and lubrication)
- e. charcoal scrubber column (replacement)

NOTE: VENT ALL ANALYZER EXHAUST GAS TO THE OUTSIDE.

Some analyzers produce high levels of ozone which first must be scrubbed with an activated charcoal column and then vented to the outside.

10.3 Zero and Span Checks (Level 2 Checks)

1. Zero and span or Level 2 checks are recommended daily.

Zero air and an NO₂ concentration that is 70% to 90% of the analyzer's range should be run each day. Those equipped with zero/span options can be set up to automatically cycle through the zero/span check each day.

For analyzers which are equipped with a daily zero and span device, check and record, in the site logbook, the most recent zero and span. Compare the most recent readings with the log entries for any zero or span drift. Dramatic shifts in zero and/or spans may require a recalibration of the analyzer.

NOTE: VENT ALL GPT BLENDERS (CALIBRATORS) AND ZERO/SPAN DEVICES TO THE OUTSIDE. UNVENTED UNITS CAN CAUSE THE BUILDUP OF UNHEALTHY CONCENTRATIONS OF NO/NO₂ AT THE SITE.

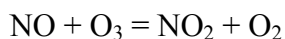
Exhaust gases must be run first through an activated charcoal column before venting to the outside.

2. For analyzers not equipped with a daily zero and span device, perform a zero check at least weekly.

An activated charcoal column with an NO catalyst can be used to produce the zero air. Because charcoal will not remove NO, a catalyst such as Purafil is required to convert NO to NO₂. The charcoal will then remove the NO₂.

11.0 Equations

Equation 5-1 - Chemiluminescent & Titration Method:



Equation 5-2 - Analyzer Measurement Principle:

$$\begin{aligned}\text{NO}_2 + \text{NO} &= \text{NO}_x (\text{NO}_y) \\ \text{NO}_x - \text{NO} &= \text{NO}_2\end{aligned}$$

Equation 5-3 - NO Concentration from the Calibrator:

$$[\text{NO}]_{\text{out}} = \frac{F_{\text{NO}} \times [\text{NO}]_{\text{std}}}{F_{\text{NO}} + F_{\text{d}} + F_{\text{o}}}$$

Equation 5-4 - NO_x Concentration from the Calibrator:

$$[\text{NO}_x]_{\text{out}} = \frac{F_{\text{NO}} \times [\text{NO}]_{\text{std}}}{F_{\text{NO}} + F_{\text{d}} + F_{\text{o}}}$$

Equation 5-5 - Desired Recorder Response:

$$\text{Desired Recorder Response (\% of scale)} = \frac{([\text{NO}]_{\text{out}} \times 100) + Z_{\text{NO}}}{\text{URL}}$$

Equation 5-6 - Observed (Measured) Concentration from the Calibration Curve (Slope):

$$\text{obsv. conc.} = (\text{mon. res.} - \text{mon. zero resp.}) \times \text{slope}$$

Equation 5-7 - Percent Difference between the observed and standard concentrations:

$$\% \text{ diff.} = \frac{\text{obsv. conc.} - \text{std. conc.}}{\text{std. conc.}} \times 100$$

Equation 5-8 - Standard Concentration of NO₂ from the Calibrator:

$$[\text{NO}_2]_{\text{out}} = [\text{NO}]_{\text{orig}} - [\text{NO}]_{\text{rem}}$$

Equation 5-9 - Concentration of NO₂ Converted:

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_y]_{\text{orig}} - [\text{NO}_y]_{\text{rem}})$$

OR

$$[\text{NO}_2]_{\text{converted}} = [\text{NO}_2]_{\text{out}} - ([\text{NO}_x]_{\text{orig}} - [\text{NO}_x]_{\text{rem}})$$

Equation 5-10 - Percent Converter Efficiency:

$$\text{Percent Converter Efficiency} = \text{slope} \times 100$$

Equation 5-11 - Standard Audit NO₂ Concentration:

$$[\text{NO}_2]_{\text{std}} = \frac{(\text{NO}_{\text{orig}} \text{ response} - \text{NO}_{\text{rem}} \text{ response} \times [\text{NO}]_{\text{orig}})}{\text{NO}_{\text{orig}} \text{ response} - \text{NO zero response}}$$

12.0 Requirements and Definitions

1. Analyzers must be recalibrated at least once every 6 months. A minimum of 2 upscale concentrations plus a zero is required for a valid calibration.
2. A valid calibration requires all calibrations points to be within $\pm 2\%$ of the full range of the analyzer (e.g., if the range is 0.5 ppm, then the measured values must be within ± 0.010 ppm of the standard. Therefore, if the standard value introduced into the analyzer is .400 ppm, the measured value must be between .390 and .410 ppm).
3. The analyzer converter efficiency must be $\geq 96\%$.
4. GPT gas blenders and NO gas cylinders must be certified by IDEM-QAS at least once every 6 months. This includes the certification of any mass flow meters used with the calibration or auditing device.
5. Data validation (Level 1) and precision audits are conducted on each analyzer once every two weeks (biweekly).

The data validation audit concentration should be between 70% and 90% of the analyzer's range. The precision audit concentration must be in the range of 0.08 ppm to 0.10 ppm.

6. The data validation limits (Level 1 audit) are:
 - a. $> \pm 15.0\%$ --- out of calibration and data is invalid
 - b. $\leq \pm 15.0\%$ and $\geq \pm 7.5\%$ --- out of calibration but data is valid
 - c. $< \pm 7.5\%$ --- in calibration and data is valid

During the NO₂ upscale audit values, residual NO in the range of .08 ppm to .12 ppm is required.

7. Accuracy audits must be performed on at least 25% of the analyzers in the network for each calendar quarter. For networks with four or fewer analyzers, an accuracy audit must be performed on each analyzer so that by the end of the year all analyzers have received one accuracy audit. Accuracy would then be calculated and reported in the 2nd and 4th quarters of the year. The QA section recommends that one accuracy audit on each analyzer be conducted every quarter. The accuracy audit will include concentrations in the following ranges:
 - a. 0.03 ppm to 0.08 ppm (Level 1)
 - b. 0.15 ppm to 0.20 ppm (Level 2)
 - c. 0.35 ppm to 0.45 ppm (Level 3)